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Review

Challenges and opportunities of lignocellulosic biomass for anaerobic digestion

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ABSTRACT

Global annual production of lignocellulosic biomass including undervalued agricultural residues and greenhouse biomass is about 181.5 billion tonnes. This undervalued biomass has a high potential to produce biogas in anaerobic digestion (AD). Among the various pre-treatment methods, hydrothermal (HT) pre-treatment of lignocellulosic biomass is a promising approach to increase biogas production in AD. However, the high carbon to nitrogen ratio (C/N) of lignocellulosic biomass is reported to be the major limiting factor for a higher biogas yield. Hence, the synergistic integration of low C/N ratio biomass with high C/N ratio lignocellulosic biomass in an AD system appears to be a logical option to enhance biogas yield. High moisture lignocellulosic biomass HT pretreatment and biogas production in AD have the potential for renewable energy production with limited use of process energy. However, hydrothermal process temperature, AD substrate C/N ratio and its inhibitory elements are important parameters for optimum biogas production. Greenhouse biomass pretreatment in hydrothermal process can produce biochar, biogas and biofertilizer, which can be used as input heat and nutrient source for greenhouses. Finally, the operation of greenhouse in this system can manage zero waste and reduce greenhouse gas (GHG) emissions and climate change.

1. Introduction

Lignocellulosic biomass is currently an undervalued biomass but it has a high potential for biogas production. Present energy research trend focuses on production of alternative energy to mitigate environmental pollution from traditional energy (Elsharnouby et al., 2013). Anaerobic digestion (AD) is the least energy-consuming process among all bioenergy production technologies with GHG emission reduction benefit (Hamawand, 2015). Lignocellulosic biomass such as agricultural residues (crop residues), wood and grass are promising sources of alternative energy (Hu and Ragauskas, 2012). Global annual production of lignocellulosic biomass is about 181.5 billion tonnes, which is an abundantly available bio-resource (Kumar et al., 2008). USA alone produces about 1.25 billion tonnes of lignocellulosic biomass annually where 30% is forest biomass (Limayem and Ricke, 2012). It was estimated that sustainably harvestable agricultural residual biomass in 2014 in Ontario would be 22.5 million tonnes (Hewson, 2010) where 12.78 million tonnes is agriculture crop residue. The estimated annual agricultural crop residue in Canada is 69.25 million tonnes, where 18.44% is in Ontario (OFA, 2013). In Canada corn, wheat, barley, canola, oats and soybean crop residue are 19.40%, 32.67%, 17.89%, 14.25%, 7.65% and 4.39%, respectively of the total crop residue. But about 62% of Ontario crop residue is corn residue (OFA, 2013).

Greenhouse biomass is also known as lignocellulosic biomass, which is the same as other agricultural crop biomass. In Ontario, 928,000 t of greenhouse biomass was produced in 2009 (Hewson, 2010). According to the Canadian Encyclopedia online report of 2015, greenhouse crop production is emerging to reduce imported foods and meet consumer's demand for fresh and healthy food in Canada (Dorais et al., 2015). Public and private research centers such as the Agriculture department, Agrifood Canada, Universities etc. are growing new varieties of different crops in greenhouses in a controlled environment. In 2014 Greenhouse crop surface land area in Canada was more than 2000 ha of which 1044 ha was in Ontario, 493 ha was in British Columbia, 235 ha was in Quebec and 116 ha was in Alberta. In 2014, about 44% of greenhouse crop lands grew vegetables, such as tomatoes (21.6%), cucumbers (11.2%), peppers (10.8%) and lettuce (0.5%). The rest of greenhouse land areas (56%) were used for agricultural, horticultural and forest plants. Greenhouses are increasing due to the increasing food supply throughout the year in Canada and their heating cost is the highest operating cost to producers. In greenhouses, heat is supplied from non-renewable fossil fuels such as oil and natural gas with high cost and environmental impact. Therefore, several greenhouses switched to biomass burning as an alternative source, which again needs extra capital investment (BioFuelNet, 2014). Till now, management of greenhouse biomass/residues through anaerobic digestion is rare in

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literature but it has the opportunity to change natural gas heating by biogas and apply digestate as nutrient to greenhouse crops if technology becomes available. Therefore, this paper is an attempt to summarize the challenges and potential pre-treatment methods of lignocellulosic biomass including greenhouse residues to produce biogas through anaerobic digestion techniques. This paper also addresses inhibitors of anaerobic digestion, their mitigation approaches and limit of inhibition for safe anaerobic digestion treatment of lignocellulosic biomass. Lignocellulosic biomass co-digestion with other substrates is also addressed to enhance biogas production. The knowledge about biogas production quality and quantity may encourage different biomass handling industries to produce renewable energy as well as GHG reduction.

2. Composition of lignocellulosic biomass

Lignocellulosic biomass is an alternative energy source, which is available to produce biofuels in North America. Wood, grass, agricultural residues, energy crops and forest residues are all types of lignocellulosic biomass (Hu and Ragauskas, 2012). Most of the plants are composed of three major components namely cellulose (38–50 %), hemicellulose (23–32 %), and lignin (10–25 %) (Sawatdeenarunat et al., 2015). Average values of these components of biomass used for biofuel production are shown in Table 1.

Cellulose fibers are stabilized laterally by hydrogen bonds which stay between hydroxyl groups and produce linear chains. Cellulose chains are stiffened by hydrogen bonds and a crystalline structure is aggregated (Pu et al., 2008). Hard wood contains higher amounts of cellulose than soft wood. Cotton fibers are simple example of cellulose (Kumar, 2010; Kambo, 2014). Hemicellulose is complex structure of carbohydrate with different types of polymer e. g. the second most common polysaccharides in nature (Saha, 2003). Unlike cellulose, hemicellulose is composed of combinations of pentoses and/or hexoses and glucose. The source of hemicellulose determines its chemical nature and in general, xylan is the dominant hemicellulose component of agricultural plants, such as grasses, straws and hardwoods (Pu et al., 2008; Kambo, 2014). Lignin is a phenolic polymer in lignocellulosic biomass and when enzyme needs to act on the carbohydrate fraction of a lignocellulosic biomass, it creates a physical barrier (Hu and Ragauskas, 2012). Softwoods contain a higher composition of lignin compared to hardwoods. Lignin provides structural strength of a plant and protects it from microbial attack.

Table 1
Composition of lignocellulosic biomass.

Biomass name	Composition (%, dry basis)			C/N ratio	References
	Cellulose	Hemicellulose	Lignin		
Rice straw	35–44	27–34	12–13	47–67	1, 2, 3, 4, 5
Cotton straw	42	12	15	–	6
Cotton stalk	31	11	28	41	7, 8
Wheat straw	38–42	20–27	20–22	50–60	1, 3, 4, 5, 9
Soybean straw	38	16	16	50	6, 10
Barley straw	38–48	21–25	11–26	71	5, 6, 10
Oats straw	33	23	21	95	6, 11
Alfalfa straw	31	10	10	47	6, 12
Rape seed straw	37	25	17	28	11, 13
Corn stover	40	25–31	14–17	50–63	1, 3, 4, 14
Corn cobs	45	25	15	123	10, 15
Sugarcane bagasse	40–45	20–24	25–30	118–150	1, 3, 4, 14
Poplar	45	21	24	103	10. 16
Pine	25–44	26–32	28–48	140	1, 6, 10
Red maple/oak	39	33	23	250	6, 10
Spruce	28–43	20–30	28–35	170	1, 6, 10
Soft wood stem	40	30	30	511	15
Switchgrass	36–45	28–30	12–26	90	1, 3, 14
Miscanthus	38–48	19–30	12–25	77	1, 5, 17, 18
Pea vines	40	10	9	120	6, 10
Green bean	17	16	8	11	19, 20
Grape stem	–	–	12	59	6, 21
Tomato pomace	39	5	11	–	6
Tomato plant	39	29	12	35	22
Cucumber plant	17	17	3	11	19, 20
Pepper plant	18	12	8	13	19, 21

1 = OFA (2013); 2 = Sun et al. (2005); 3 = Karthikeyan and Visvanathan (2012); 4 = Divya et al. (2015); 5 = Sawatdeenarunat et al. (2016); 6 = Cornell composting (2015); 7 = Silverstein et al. (2007); 8 = Munir et al. (2009); 9 = Silva and Rouau (2011); 10 = Saidur et al. (2011); 11 = Lehtomaki et al. (2008a, 2008b); 12 = Sawatdeenarunat et al. (2015); 13 = Díaz et al. (2010); 14 = Saha (2003); 15 = Chandra et al. (2012a, 2012b); 16 = Sannigrahi et al. (2010); 17 = Hodgson et al. (2011); 18 = De Jong et al. (2003); 19 = Callejón-Ferre et al. (2014); 20 = Callejón-Ferre et al. (2011); 21 = Masiá et al. (2007); 22 = Font et al. (2009)

Table 2
Growth of AD in Europe and North America (CBA, 2017; ABC, 2017; EBA, 2016).

Country/ Province	Number of installed AD in operation								
	2012			2014			2016		
	Farm	Other	Total	Farm	Other	Total	Farm	Other	Total
Ontario	4	8	12	35	9	44	36	35	71
Canada	13	117	130	47	120	167	51	135	186
USA	192	1828	2020	239	1877	2116	259	1953	2212
Europe	–	–	13812	–	–	17240	–	–	17358
Germany			8700			10786			10846

3. Growth of AD plants in North America and Overall

Installation of AD plants has increased rapidly in Ontario since 2012 as a result of the introduction of the feed in tariff (FIT) program for farm level electricity production in combined heat and power (CHP) system. The growth of biogas plants in North America and Europe is shown by number in Table 2. There were only 4 AD plants in Ontario until 2012, which was rapidly increased to 35 in 2014 and 36 in 2016 at farm level due to the introduction of FIT in 2013. Ontario government changed policy to allow farm ADs to use up to 50% off-farm substrate in 2013. Now farmers have the opportunity to earn 20 \$ t^{-1} to 50 \$ t^{-1} extra for receiving tipping fee from off-farm substrates. At present, the city of Toronto of Ontario pays about 120 \$ t^{-1} to landfill owners as a tipping fee for their waste diversion. This data was collected during a visit of Toronto AD plant. Until the end of 2016, the total number of AD installed in Ontario was 71 whereas it was 186 in Canada. In USA and Canada, AD is mostly used for manure treatment at farm and municipal waste water treatment. In Europe, the number of installed AD in 2012 was 13812 of which 8700 was in Germany. This number was increased to 17358 in Europe and 10846 in Germany in 2016. Several AD plants are used for landfill gas mitigation purposes. Only one municipal food waste processing wet mesophilic AD plant is being operated in North America and it is in Toronto, Canada.

Food waste co-digestion with manure is being encouraged in farm AD to use its extra capacity, existing infrastructure and expertise. Farm ADs in Ontario are now receiving tipping fee and FIT benefit. Opportunity has been created for farm AD owners to produce renewable energy by receiving carbon credit in Canada, Europe, and USA. Asian and African countries use limited number of industrial sized (about 10,000 m^3 volume) biogas plants but they are using small scale locally built biogas plants for cooking and other household purposes. China, India and Nepal started national biogas program around 1950 and by 2009 they had about 17 million, 12 million and 190 thousand biogas AD plants made of masonry materials of 4 m^3 to 10 m^3 volume (Fulford, 2017). The African Biogas Partnership Program built 3660 biogas plants in Africa from 2009 to 2015 using the technical assistance of the Netherlands Development Organization (Berhe et al., 2017). According to the report of Subedi, P.S. (2013) of Winrock International, Bangladesh built 23611, Pakistan built 2097, Indonesia built 5572,

Vietnam built 140698, Cambodia built 17450 and Laos built 2715 domestic biogas plants by 2012.

4. Challenges of lignocellulosic biomass in AD treatment

Lignocellulosic biomass including greenhouse residues have high methane potential for anaerobic digestion but the complexity of their structure (contains 10–25% lignin) inhibits anaerobic digestion process (Sawatdeenarunat et al., 2015). Major crops grown in greenhouses are tomato, cucumber, paper and grape and their C/N ratio values are 35, 11, 13 and 59, respectively (Table 1). These values are quite favourable ranges for AD. But for presence of lignin in greenhouse biomass, their pretreatment is needed before use in AD for biogas production. Research in this area is needed for bio-methane production. Produced bio-methane can be used later in CHP to produce energy. This energy can be used as the heat source of greenhouses and its waste CO_2 can be used as the greenhouse input. During AD process, the methane yield is decreased for the increase in biomass particle size (Yang et al., 2015). Although solid state AD (SS-AD) installation has been increased in the past decade for its low cost and environment-friendly technology, its methane yield and instability of the process are still two major challenges to run it commercially (Ge et al., 2016). The complex structure of lignocellulosic biomass may be one reason, which can be overcome by pretreatment of feedstock and its co-digestion with other feedstock (Yang et al., 2015). Currently, bio-refineries are attempting to use their bio-refinery waste as feedstocks for AD process for biogas production. The integration of AD into bio-refinery plants for additional bioenergy production is important for future direction (Sawatdeenarunat et al., 2016). Therefore biogas production from lignocellulosic biomass is a big challenge and to overcome it, pretreatment is essential. On the other hand, currently installed AD plants are of the same design as waste water treatment plant digesters, which were designed without pretreatment facilities. But they are being used for lignocellulosic biomass digestion (Sawatdeenarunat et al., 2015). Pretreatment of lignocellulosic biomass is discussed in the next section.

4.1. Recalcitrance of AD feedstock

Biogas raw materials are abundant as agricultural residue (rice straw, wheat straw, corn straw), greenhouse residues, agro-industrial waste, grasses, hardwood and softwood, which are called lignocellulosic biomass. This biomass can work as raw materials of biogas production and they contain cellulose, hemicellulose and lignin (Berglund Odhner et al., 2012). But the complex structure and lignin content of lignocellulosic biomass create recalcitrance in AD (Hu and Ragauskas, 2012). Pretreatment is essential for cellulosic biomass to alter cellulose and hemicellulose (but not lignin, because it produces AD inhibitory phenolic compounds) to more accessible enzymes (Zheng et al., 2009; Mosier et al., 2005). After pretreatment, biomass becomes more porous but it may produce inhibitory substances to anaerobic microbes (Berglund Odhner et al., 2012). A unique pretreatment method for all lignocellulosic biomass for different biofuel production is not available. Therefore various pretreatment methods are discussed in the next section.

4.1.1. Methods of pretreatment

Pretretment methods for biogas production from lignocellulogic biomass can be divided into mechanical, thermal, chemical, biological and hybrid combinations (Tables 3 and 4). Chopping, milling, grinding and blending are examples of mechanical pretreatment. Explosion of steam to biomass and thermal hydrolysis are examples of thermal pretreatment. Hydrolysis using acid, alkali and oxidising agents are chemical pretreatment and fungi used during methane production is biological pretreatment. Lignocellulosic biomass can be a potential substrate after appropriate pretreatment for biogas production (Sawatdeenarunat et al., 2015).

In thermal pretreatment process at 150–180 °C, the hemicellulose part is solubilized and several organic acids are produced (Garrote et al., 1999). However, in this case there is a risk of production of inhibitory products. Some phenolic (furfural) and heterocyclic compounds like hydroxyl methyl furfural (HMF) are produced during acidic thermal pretreatment, which are inhibitory substances for AD (Negro et al., 2003; Ramos, 2003). Another thermal process is steam explosion where high temperatures (up to 240 °C) and pressures (up to 33.4 bar or 3.34 MPa) are applied for several minutes. Long pretreatment time produces more inhibitory products. Dilute acid hydrolysis such as sulfuric and nitric acid at 160 °C to 220 °C is used for lignocellulosic biomass for few minutes (Digman et al., 2010; Li et al., 2010). Concentrated acid can be used at low temperatures but it has a corrosive effect on reactor (Brown and Brown, 2013). There is a risk of furfural and HMF production in this process. Alkali hydrolysis refers to the use of various bases like NaOH, KOH, $Ca(OH)_2$, aqueous ammonia and NH_4OH (Silverstein et al., 2007; Zheng et al., 2009; Zheng et al., 2014; Abdi et al., 2000; Carrillo et al., 2005; Chang et al., 2001; Kim and Holtzapple, 2005; Kim et al., 2003) to avoid inhibition. On the other hand, oxidative agents such as hydrogen peroxide, ozone and oxygen or air are used for delignification of biomass but they can create inhibition in digestion process (Hon and Shiraishi, 2000). As an alternative of steam explosion, hydrothermal treatment (wet oxidation) is being widely used. Here, air or oxygen works as an oxidising agent to dissolve the suspended component of biomass in water above 120 °C for a period of 30 min (Palonen et al., 2004). In the case of the industrial process of biomass containing high organic matter, this hydrothermal treatment is used at high temperatures (150–350 °C) and at pressure of 5–20 MPa (Jorgensen et al., 2007). Wet oxidation ruptures the crystalline cellulosic structure of biomass, which is suitable for hard wood and wheat straw (Panagiotou and Olsson, 2007). In the case of biological treatment, fungi are used to disrupt the cell wall of biomass (Komilis and Ham, 2003).

4.1.2. Evaluation of pre-treatment methods

Table 5 is prepared based on the pretreatment methods summarised in Tables 3 and 4. Among all pretreatment technologies, hydrothermal with alkali pretreatment appears to be a favourable technology for lignocellulosic biomass (non-woody such as crop residues) conversion into biogas in AD process. This pretreatment can help to keep the feedstock's pH close to neutral, which depends on the amount of alkali added. The alkali addition should not exceed the inhibitory limit. As an example, the maximum value of Na of 3000 mgL^{-1} and K of 12000 mgL^{-1} are inhibitory to AD (Tchobanoglous et al., 2014). Lignocellulosic biomass with higher moisture content is always considered as an undervalued biomass and it saves drying energy when it used for hydrothermal pretreatment process.

4.1.3. Severity during acid hydrolysis of lignocellulosic biomass

In the case of acid pretreatment, some AD inhibitory products such as furfural and HMF are produced, which create severity. In the case of acid pretreatment, dried milled biomass is presoaked in water and then it is submersed in an acidic solution at a certain temperature for a certain time and then it is neutralised before digestion (Bensah and Mensah, 2013). This pretreatment process is normally affected by temperature, reaction time, liquid solid ratio, particle size and concentration of acid. These factors are responsible for severing the process, which is represented by a severity factor. An index, namely combined severity (R_0' or CS) is used to assess the effect of time, temperature and pH (Chum et al., 1990) where severity factor R_0 includes time and temperature effects. Here $CS = \log R_0 - pH$ and $R_0 = t.e^{(T-100)/14.75}$ where t is the time of the reaction in minutes and T is the reaction temperature in degree centigrade (Jeong and Oh, 2011; Abatzoglou et al., 1992). For hydrothermal pretreatment, rice husk produced glucose and arabinose (xylan product), which stayed fairly constant with severity (Vegas et al., 2008). In the case of hydrothermal

Table 3
Biogas production after pretreatment of woody biomass in wet AD.

Substrate name	Pretreatment		Digestion		Methane yield	Reference
	Type	Condition	Type	Time (days)		
Eucalyptus	Mechanical	wood chip	Mesophilic	14	0-14 Lkg^{-1} TS	Nakamura and Mtui (2003)
	Thermal	Wood chip in hot water at 125 °C for 20 min	Mesophilic	14	124 Lkg^{-1} TS	
		Steam explosion to chip at 25 atm,3 min	Mesophilic	14	194 Lkg^{-1} TS	
	Chemical	Wood chip in 1% NaOH with hot water at 125 °C for 20 min	Mesophilic	14	134 Lkg^{-1} TS	
Japanese cedar wood and Spruce	Mechanical	Wood chip	Mesophilic	20–60	0	Take et al. (2006), Amirta et al. (2006), Teghammar et al. (2012), Mirahmadi et al. (2010) and Dererie et al. (2011)
		Milled wood < 1 mm	Thermophilic	45	30–80 Lkg^{-1} VS	
	Thermal	Steam explosion to chip at 4.5 MPa at 258 °C for 5 min	Mesophilic	20–60	180 Lkg^{-1} TS	
	Chemical	Chip 6% Spruce wood in N-Methylemorpholine N-oxide (NMMO) solution in oil bath at 130 °C and 1 atm for 15 h	Thermophilic	45	150 Lkg^{-1} VS	
		Milled 6% Spruce wood NMMO solution in oil bath at 130 °C, 1 atm, 15 h	Thermophilic	45	295 Lkg^{-1} VS	
		7% NaOH at 5 °C, for 2 h	Thermophilic	30	50 Lkg^{-1} VS	
	Biological	Fungal for 8 weeks	Mesophilic	20–60	0	
Birch tree	Mechanical	Wood chip	Thermophilic	30	250 Lkg^{-1} VS	
	Chemical	7% NaOH at 100 °C for 2 h	Thermophilic	30	649 Lkg^{-1} VS	

acid pretreatment of rape straw at CS value of 1.3, 82.37% XMG (xylan + mannan + galacta) and 77.8% glucose can be recovered (Jeong and Oh, 2011). An experiment was carried out by Lee and Jeffries (2011) for determining the efficiencies of acid catalysts at a constant CS value for three acidic hydrolysis pretreatment of lignicellulosic biomass such as sulfuric acid, oxalic acid and maleic acid. Among these three acids, maleic acid released the highest amount of sugar and also produced the highest amount of HMF and furfural. Oxalic acid produced the second highest value of these materials. Sulfuric acid produced the least amount of glucose, furfural and HMF among these three acid catalysts. Anaerobic microbes have several restrictions to work properly and these restrictions are called inhibition, which need to be mitigated and they are discussed in the next section.

Table 5
Evaluation of lignocellulogic biomass pretreatment methods for biogas production.

Biomass type	Pretretment effect on biogas production				
	Mechanical	Thermal	Hydrothermal	Chemical (alkali) and thermal	Chemical (alkali) and hydrothermal
Woody	Lowest	low	medium	high	high
Non-woody (crop resi-dues)	Lowest	low	medium	high	highest

4.2. Inhibition during anaerobic digestion process

Common inhibitors present in substrate during anaerobic digesters are ammonia, sulfide or sulfur, light metals, heavy metals, oxygen and organic compounds. Poor operational conditions also prevent the anaerobic digestion process (Dupla et al., 2004). During anaerobic digestion, acid forming bacteria and methane forming microorganisms (archaea) differ in their physiological and nutritional need, which needs to primarily balance the stability of the process (Demirel and Yenigün,

Table 4
Biogas production after pretreatment of straw biomass in wet AD.

Substrate name	Pretreatment		Digestion		Methane yield Lkg^{-1} VS	Reference
	Type	Condition	Type	Time (days)		
Rice straw, corn straw, corn stover, switch grass, wheat straw	Mechanical	Chopped into 3–5 cm	Mesophilic at 22 °C	120	240	Sawatdeenarunat et al. (2015), Lei et al. (2010), Hjorth et al. (2011), Zhong et al. (2011), Sharma et al. (1998) and Brown et al. (2012)
			Mesophilic	28–30	117–190	
		Size reduced to 0.088 mm	Mesophilic	60	365	
		Grounded to 25 mm	Mesophilic	24	200	
Green leaves and yard waste	Non-treated	As collected	Mesophilic	30	41–55	
	Chemical	8% NaOH	Mesophilic	30	472	
		5% Ammonia	Mesophilic	30	316	
		4% Urea	Mesophilic	30	178	
		7.5% Rice straw in NMMO solution heat in oil bath at 130 °C and 1 atm for 1 h	Thermophilic	45	212	
		Grounded to 25 mm at 130 °C with Ammonia	Mesophilic	24	245	

2002).

4.2.1. Ammonia inhibition

During the anaerobic digestion process, for the biological degradation of nitrogenous matters, ammonia is produced in both ammonium (NH_4) and free ammonia (NH_3) forms where free ammonia acts as a strong inhibitor in anaerobic digester (Yenigün and Demirel, 2013). Free ammonia nitrogen (FAN) production during AD process varies with the total ammonium nitrogen (TAN) and pH value of the substrate. Glucose degradation during AD process inhibits about 70% for 3500 mgL^{-1} TAN at pH 8.0 (Fujishima et al., 2000) and it becomes severe at 6390–7460 mgL^{-1} TAN at pH 7.4-7.5 for 197–230 mgL^{-1} FAN (Nordberg et al., 2007). An AD research was carried out with alfalfa silage at pH 7.2–7.8 where TAN was increased from 1600 mgL^{-1} to 5000 mgL^{-1} by recirculating effluent, which showed severe inhibition in AD process (Nordberg et al., 2007). Municipal organic waste digestion can produce optimum methane at pH 7.9 and 3300 mgL^{-1} TAN. But it is reduced to half (50% inhibited) when TAN concentration increased to 5500 mgL^{-1}. In the case of dewatered sludge digestion at pH 8.0, TAN 3000 mgL^{-1} and FAN 400 mgL^{-1}, biogas production was moderately inhibited but the inhibition observed severity at TAN and FAN value of 4500 mgL^{-1} and 800 mgL^{-1}, respectively (Duan et al., 2012). In the case of organic fraction of MSW digestion, 50% inhibition was observed for 3860 mgL^{-1} TAN and 215 mgL^{-1} FAN for mesophilic digester and 5600 mgL^{-1} TAN and 468 mgL^{-1} FAN for thermophilic digester (El Hadj et al., 2009). In AD process C/N ratio plays an important role for TAN and FAN concentration of substrate, which works for NH_3 inhibition. In co-digestion of wheat straw and manure, a C/N ratio of 25, 30 and 35 provides a stable TAN value of 712 mgL^{-1}, 604 mgL^{-1} and 444 mgL^{-1} and FAN value of 9.1 mgL^{-1}, 7.5 mgL^{-1} and 2.2 mgL^{-1}, respectively. But for a C/N ratio of 15 in the same condition, TAN and FAN value is increased to 2614 mgL^{-1} and 223 mgL^{-1}, respectively (Wang et al., 2012). Optimization of C/N ratio of substrate can be achieved by the co-digestion process. FAN is a powerful inhibitor, which is produced during AD process at pH values higher than 7.4, higher temperatures like thermophilic condition and lower C/N ratio e.g. lower than 20 (Yenigün and Demirel, 2013).

4.2.1.1. Counteract and recovery of ammonia inhibition. Previous studies indicate that digestion toxicity can be minimized by lowering the pH and FAN of AD substrate. To maximize biogas production, the concentration of TAN and FAN can be controlled by adjusting C/N ratio and pH value of substrate. At a C/N ratio of 15 and pH 6.5, mesophilic AD provides the best results (Shanmugam and Horan, 2009). For recovery of ammonia inhibition, addition of diluted manure substrate in AD can produce a high amount of methane, which seems to be the most stable recovery process of ammonia (Callaghan et al., 1999; Nielsen and Angelidaki, 2008). An AD research was conducted by Karthikeyan and Visvanathan (2012) with various substrates such as green waste, food waste, fruits and vegetable waste and paper waste with a constant organic loading rate (OLR) of 7–10 kg VS/m^3/day for various retention times up to 19 days, where ammonia inhibition (accumulation) reduced to 30% for C/N ratio of 32 compared to C/N ratio of 27. The authors recommended maintaining higher OLR to overcome ammonia inhibition. Slaughterhouse waste substrate with 6000–7400 mgL^{-1} TAN in AD with hollow fiber membrane can reduce 70% of FAN concentration, which can stabilize the AD process to increase biogas production (Lauterböck et al., 2012). Air stripping is a proven technology for mitigating high ammonia concentration during AD process (Kabdasli et al., 2000). Use of inert materials such as zeolite, activated carbon, clay etc. in substrate can create immobilization of microorganism and reduce ammonia inhibition where natural zeolite works as ammonium ionic exchanger and reduces the pH of substrate (Ho and Ho, 2012; Hansen et al., 1998).

4.2.2. Sulfide or sulfur inhibition

During an AD process sulfur remains in sulfate form, which is reduced to sulfide by sulfate reducing bacteria (SRB). High sulfur present in substrate is an inhibitor of AD process. Methanogens i.e. methane producing bacteria (MPB) have tolerance with SRB present in the AD substrate along with other inhibitory elements (NREL, 2013). SRB works on sulfate and produces sulfide. The threshold value of C/SO_4 ratio is 1.60 of an AD substrate for methane production, which is 1400 mgL^{-1} SO_4 (Siles et al., 2010).

4.2.2.1. Control of sulfide/sulfate toxicity. SRB actions during acidogenic phase of sucrose AD in a laboratory was studied by Mizuno et al. (1998). They found about 90% of sulfur removal efficiency at 6.0–6.5 pH range and 1200 mgL^{-1} value of sulfate concentration but in the case of high sulfur concentration (> 2400 mgL^{-1}), this efficiency was reduced to 60%. Acidogenic stage can reduce sulfur and the use of a separate reactor in this phase can reduce sulfur compound at an earlier stage. To remove volatile sulfur from the AD substrate, an experiment was carried out by Dhar et al. (2011) with pretreatment of substrate at 60 °C temperature in the presence of 0.6 mg H_2O_2 and 1.5 mg $FeCl_2$ per mg sulfide in a continuous AD process of activated sludge. For this pretreatment H_2S, dimethyl sulfide (DMS) and methanethiol (MT) concentrations of biogas were reduced to 70%, 40% and 10%, respectively. For this controlling measures methane production rate was increased to 20% compared to non-treated substrate. Prediction of H_2S production of an AD process can be determined by C/S ratio of a bioenergy feedstock (Peu et al., 2012) and H_2S in raw biogas can be kept at 2% (volume/volume) when substrate's C/S ratio can be maintained at 40 or higher.

4.2.3. Metal inhibition

In the biological field, toxicity of salt to microorganism has been studied for several decades. Bacterial cells become dehydrated for osmotic pressure due to high salt (sodium toxicity) present in substrate (Yerkes et al., 1997). Light metals including potassium, sodium, magnesium, aluminium and calcium are present in the influent of anaerobic digester. With the breakdown of organic matters (biomass) or adjustment of pH, these metals can remove into substrate and their cations create toxicity to the AD process (Grady et al., 2012). Depending on their concentration value, substrate changes from low toxicity to severe toxicity. Heavy metals are not biodegradable but they can accumulate in substrate in a toxic concentration amount. Heavy metals such as Cr, Co, Cu, Zn, Cd, Ni and Fe can disrupt the enzyme function (Chen et al., 2008).

4.2.4. Organic content inhibition

Anaerobic processes are also inhibited by various organic compounds and their several organic chemicals. During the acid (NHO_3) pretreatment in high temperature of biomass, hydroxyl methyl furfural (HMF) and furfural are generally produced (Park et al., 2015), which are inhibitors in AD process. The concentration of HMF becomes the highest during 0.5% HNO_3 pretreatment and the highest concentration of furfural is produced by 1% HNO_3 pretreatment of biomass (rice straw). If HNO_3 concentration becomes greater than 2%, furfural and HMF concentration are reduced due to their break down into formic acid, levulinic acid, etc. (Table 6). Furfural is a stronger inhibitor than HMF in AD (Modig et al., 2002). Therefore, biomass pretreatment with 0.55 HNO_3 will create a moderate inhibition to AD. Adjustment of pH by NaOH will cause nitric acid destruction to produce NO_3,which will increase nitrogen content of substrate i.e, C/N ratio will be reduced (Khalid et al., 2011) and it will finally affect the biogas production. Microbial acclimation with other inhibitory substances is also inhibitors to AD process. Lignin derivatives are highly toxic to methanogens when they are present with aldehyde groups (Chen et al., 2008).

Table 6
Furfural and HMF for nitric acid pretreatment of biomass (Park et al., 2015).

HNO_3 concentration (%)	Furfural production (mgL^{-1})	HMF production (mgL^{-1})	Solid recovery (%)
0	–	–	100
0.2	–	480	51.74
0.5	430	1140	51.18
1	1090	870	42.98
2	90	100	–
3	70	40	–

Table 7
Inhibition limit of substances for potential cause in AD (Tchobanoglous et al., 2014; EPA, 2006).

Substance	Moderately inhibitive ($mgL^{-1)}$	Strongly inhibitive (mgL^{-1})
Calcium	1500–4500	8000
Ammonia Nitrogen	1500–3000	3000
Sodium	3500–5500	8000
Magnesium	1000–1500	3000
Potassium	2500–4500	12000
Sulfur	200	200
Zinc	–	1.0 (soluble)
Copper	–	50–60 (total)
Nickel	–	30 (total)
Chromium	–	180–420 (total)
Chromium VI	–	200–250 (total)

4.2.5. AD inhibition limit

Various researches have been suggested to ensure the inhibitory substances are kept below inhibition limit during AD process. Elemental determination of substrate/broth can ensure the inhibition limit shown in Table 7 of AD microbial positive activity (EPA, 2006). Ammonia (both NH_4 and free NH_3 forms) can cause inhibition in AD system (Song et al., 2005). AD set up in mesophilic temperature can control this inhibition (Komemoto et al., 2009). In AD digester, SRB produces sulfide from sulfate mostly in the same condition of methane production, which decelerates methanogenic activity and produces poisonous H_2S gas. This H_2S gas creates problem for AD plant operators as well as power generating engine (Chen et al., 2008).

5. Opportunities for enhancement of biogas production in anaerobic digestion

AD feedstocks are converted in four individual but tightly inter related steps to produce final product of biogas (Song et al., 2005). The first step called hydrolysis is the most important step where biomass is hydrolysed by facultative and obligate bacteria to produce water soluble monomers from AD feedstock. For the strong structure of lignocellulosic biomass and presence of lignin, it is difficult for facultative bacteria to hydrolyse it properly. This may be one reason for low biomass production in SS-AD of non-treated biomass. The low methane yield of SS-AD is the primary challenge of a SS-AD operation (Yang et al., 2015). But there is an opportunity to produce maximum amount of biogas if lignocellulosic biomass can be converted into water soluble organics of cellulose and hemicellulose derivatives without degrading its lignin content. A proper hydrothermal pretreatment can solve this problem. On the other hand, for maintaining optimum C/N ratio of 20–30 of AD feedstock, co-digestion of high C/N ratio containing biomass with low C/N ratio containing biomass can enhance biogas production. These two opportunities are discussed in next two subsections.

5.1. Hydrothermally pretreated lignocellulosic biomass is an opportunity for AD

Hydrothermal pretreatment of biomass is a new approach, which is performed in a water submersed condition. Submersed biomass is heated in a confined system at 180–260 °C temperature for 5–240 min (Fig. 1). Hydrothermal liquid of lignocellulosic biomass can produce biogas in AD process (Fig. 2).

In the hydrothermal process, water creates reactant, solvent and reaction environment even in subcritical condition. When biomass in water is heated up, cellulose ($C_6H_{10}O_5$) is hydrolysed into glucose (Kruse et al., 2013).

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \quad (1)$$

Then glucose ($C_6H_{12}O_6$) is converted into hydrochar (coal like carbon) and water. Here, an exothermal reaction is occurred (Titirici and Anietti, 2010).

$$C_6H_{12}O_6 \rightarrow C_6H_4O_2 + 4H_2O \quad (2)$$

A typical HTC experiment of cellulose gave the following equational results (Libra et al., 2011).

$$C_6H_{12}O_5 \rightarrow C_{5.25}H_4O_{0.5} + 0.75CO_2 + 3H_2O \quad (3)$$

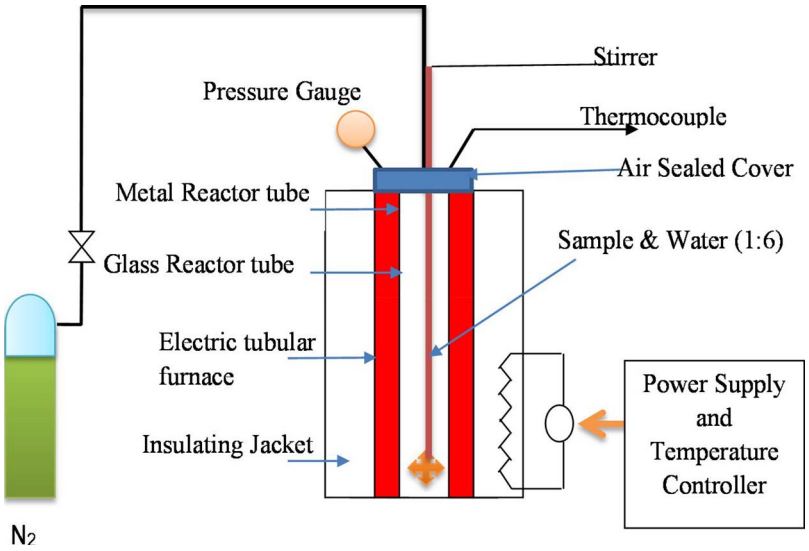

Fig. 1. Hydrothermal pretreatment of lignocellulosic biomass in subcritical reactor.

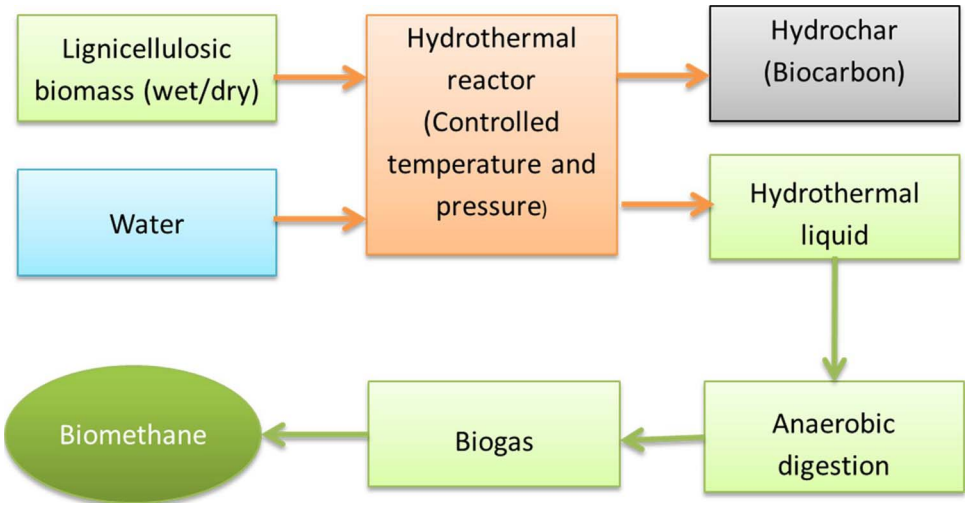

Fig. 2. Hydrothermal pretreatment and biogas production from lignocellulosic biomass.

Biomass has complexity and heterogeneity and it can not be a well-defined reactant. Therefore Eq. (3) is not considered for reaction products of hydrothermal liquid organic of a biomass (Libra et al., 2011). In the hydrolysis stage, cellulose is converted into glucose; hemicellulose is converted into xylose ($C_5H_{10}O_5$), arabinose ($C_5H_{10}O_5$), furfural ($C_5H_4O_2$) and HMF ($C_6H_6O_3$) in liquid. But Furfural and HMF are inhibitory to AD microbes. On the other hand, in liquid media, lignin polymers such as syringaldehyde ($C_7H_4O_2(OCH_3)_2$) and vanillin ($C_7H_5O_2(OCH_3)_1$) are produced, which are hard to degrade by anaerobic microbes (Barakat et al., 2012). According to above cases consideration for anaerobic digestion, glucose is easily converted into methane and CO_2, which is shown in Eq. (4) (Panagiotou and Olsson, 2007).

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \quad (4)$$

For the hydrothermal pretreatment of biomass, biogas production is increased. A research result showed that biogas (from rice straw) production can be increased to 132% and 226% by alkali (NaOH) and hydrothermal (HT) pretreatment followed by alkali, respectively, compared to its untreated digestion (Chandra et al., 2012a, 2012b). HT process produces solid (hydrochar), liquid (aqueous soluble) and gaseous (mainly CO_2) products. HT liquid has potentiality (contain about 40% of organic carbon at 260 °C temperature) to be used for anaerobic digestion (Kambo, 2014; Wirth and Mumme, 2014) by adjusting its pH from 2.5 − 3.5 to neutral. It is mandatory to add NaOH to slurries produced after hydrothermal pretreatment of biomass to maintain optimum pH for AD treatment (Libra et al., 2011). Phenolic compounds have inhibition in anaerobic condition both in gas production and autoxidation in wet conditions (Kayembe et al., 2013). For compounds with low pH (2.5–3.5) value (Kambo, 2014) and high C/N ratio of HT pretreated lignocellulosic biomass, their co-digestion with low C/N ratio biomass can maintain optimum C/N ratio of AD digester to increase biogas production.

Hydrothermal pretreatment of rice straw at 200 °C and 1.55 MPa water vapor pressure for 10 min was carried out by Chandra et al. (2012a, 2012b) to enhance methane production. Authors compared this result with 3% NaOH pretreatment of rice straw at 37 °C (mesophilic temperature) for 120 h. Authors observed that the pH value of hydrothermal process led to an increase in temperature to 225 °C and found that for the same condition, pH decreased from 4.93 to 3.97. They pointed out the reasons behind pH drop for oxidation of biomass containing sulfur, phosphorous and other minerals. However, the authors increased pH value to neutral (7.0) by adding 5% NaOH and the pretreated biomass was set for mesophilic anaerobic digestion for 60 days where C/N ratio, TS concentration and substrate/inoculum ratio were 25, 5.0% and 1, respectively. The hydrothermally pretreated biomass can produce 2 times of biogas by volume compared to untreated biomass. The methane composition of hydrothermally pretreated biomass is 60% of the produced biogas. Biogas production from untreated, NaOH pretreated and hydrothermal pretreated of rice straw were 140.0 Lkg^{-1} VS, 184.8 Lkg^{-1} VS and 315.9 Lkg^{-1} VS, respectively (Chandra et al., 2012a, 2012b).

Till now the undervalued biomass such as food waste and greenhouse waste (lignocellulosic biomass) require payment of tipping fee to bury them in landfills where GHGs (CH_4 and CO_2) are produced after decomposition. But it has opportunity to produce CH_4 in AD for various applications as a renewable energy source. For high C/N ratio and lignin content, lignocellulosic biomass alone will face inhibition problems during individual AD treatment. Another issue is that there is not much concern about greenhouse biomass management in AD process. HT pretreatment with NaOH or KOH of lignocellulosic biomass is required to increase its biogas potentiality.

5.1.1. Estimation of hydrothermal process input energy

The energy required for heating up the biomass and water mixture of hydrothermal cylinder can be calculated as follows (Anastasakis and Ross, 2015):

$$E_{HT} = Q\ (kJ) = C_p\ (kJkg^{-1}K^{-1}) \times m\ (kg) \times dT\ (K) \quad (5)$$

Where, Q is the amount of heat energy gained or lost by biomass and water of HT cylinder in kJ, m is its mass in kg, C_p is the specific heat capacity of biomass and water mixture in $kJkg^{-1}K^{-1}$ and dT is its temperature change in K.

The hydrothermal material is the mixture of biomass (dry matter) and water. Therefore, C_p of the mixture can be calculated as follows:

$$C_p = C_{p,biomass} \times wt_{biomass}\ (\%) + C_{p,water} \times wt_{water}\ (\%) \quad (6)$$

C_p of water at 25 °C is 4.18 $Jg^{-1}K^{-1}$, at 200 °C is 4.51 $Jg^{-1}K^{-1}$ and at 250 °C is 4.87 $Jg^{-1}K^{-1}$ (Anastasakis and Ross, 2015). For the simplicity of calculation, C_p value of 4.51 $Jg^{-1}K^{-1}$ of water can be considered for a biomass hydrothermal process. According to the research of Dupont et al. (2014), the heat capacity of corn residue (CR) at 40 °C (313 K) is 1.395 $Jg^{-1}K^{-1}$, which is linearly increased to 1.610 $Jg^{-1}K^{-1}$ until at 80 °C (353 K) and then decreased at a constant rate until 170 °C (443 K) for exothermal reaction and again increased until 240 °C (513 K) at quite similar rate for endothermal reaction. After 240 °C the heat capacity of biomass becomes constant. Therefore, for the simplicity, energy requirement to heat up of biomass from 80 °C to 240 °C is not considered. But for heating up of water from 80 °C to 240 °C, energy is required. For hydrothermal treatment, the average value of C_p, for CR can be of $[1.395 \times 15 + \{1.395 + (1.610 - 1.395)/40)\} \times 40]/55 = 1.399\ Jg^{-1}K^{-1}$. From 25 °C to 240 °C considerable dT value is 55.

Table 8
Biogas production in co-digestion of biomass with other organic in wet AD.

Substrate name	Co-digestion substrate		Digestion		Methane yield (Lkg^{-1} VS)	Reference
	Name	Condition	Type	Time (days)		
Rice straw, Wheat straw, Barley straw, corn straw	Swine manure	Continuous flow	Mesophilic	30	300–350	Moeller and Andersen (2006), Lehtomaki et al. (2008a, 2008b), Demirbas (2006) and Ye et al. (2013)
	Cattle manure	Continuous flow	Mesophilic	100–120	340–380	
		Batch	Mesophilic	28	200	
Switch grass	Swine manure	Dry digestion	Thermophilic	62	337	Ahn et al. (2010)
Grass silage	Cattle manure	Semi-continuous	Mesophilic	20	268	Lehtomaki et al. (2007)
Crop silage	Cattle manure	Semi-continuous	Mesophilic	20	249	Sawatdeenarunat et al. (2015)
Corn Stover	Chicken manure	Semi-continuous	Mesophilic	24	223	Li et al. (2014)

Therefore, total consumed energy of a hydrothermal process will be E_{HT} + water heating up energy after 80 °C (Eq. (7)).

In weight basis at 5% dry CR and 95%water in the hydrothermal process C_p value can be calculated as follows:

$C_p = 1.399 \times 0.05 + 4.51 \times 0.95\ Jg^{-1}K^{-1} = 4.35\ Jg^{-1}K^{-1}$.

$E_{HT} = Q\ (kJ) = 4.35\ Jg^{-1}K^{-1} \times 55\ K = 239\ kJkg^{-1}$ of HT input slurry = $4.78\ MJkg^{-1}$ of dry CR.

Heating up of water from 80 °C to 240 °C need energy of $4.51 \times 0.95 \times 160 = 685.52$ kJ, which needs to add with required energy.

$$E_{total} = E_{HT} + E_{water} \quad (7)$$

Here, E_{total} is the total required energy for a hydrothermal process and E_{water} is the energy required to heat up water alone from 80 °C to 240 °C.

The required energy to run the hydrothermal process depends on the ratio of biomass and water. The increase of biomass content would decrease the E_{HT} value. An increase in the amount of water in hydrothermal reactor increases the E_{HT} value for higher required energy for heating due to high specific heat capacity of water (Anastasakis and Ross, 2015). Therefore, determination of biomass and water ratio for minimum E_{HT} value is important for a hydrothermal process. It also reduces the total input energy of a hydrothermal process. In two similar researches, corn husk to water ratio of 1:12 and miscanthus to water ratio of 1:6 in hydrothermal process were used for good quality biochar production (Minaret and Dutta, 2016; Kambo and Dutta, 2015). Following the above C_p calculation, it can be estimated that for the hydrothermal process of 240 °C for 30 min with 5%, 7.5%, 10%, 12.5% and 15% CR (dry) composition in water will require energy (E_{HT} value) of 4.78 $MJkg^{-1}$, 3.14 $MJkg^{-1}$, 2.31 $MJkg^{-1}$, 1.81 $MJkg^{-1}$ and 1.48 $MJkg^{-1}$ of dry CR plus water heating up energy from 80 °C to 240 °C in each case, respectively to run the hydrothermal process. The heating up of water required energy for these compositions of hydrothermal process are estimated to 685.52 kJ, 667.48 kJ, 649.44 kJ, 631.40 kJ and 613.36 kJ of energy, respectively for above compositions, which are equivalent to 13.71 $MJkg^{-1}$, 8.90 $MJkg^{-1}$, 6.50 $MJkg^{-1}$, 5.05 $MJkg^{-1}$ and 4.09 $MJkg^{-1}$ of dry CR, respectively. The total hydrothermal process running energy would require of 18.50 $MJkg^{-1}$, 12.04 $MJkg^{-1}$, 8.80 $MJkg^{-1}$, 6.86 $MJkg^{-1}$ and 5.57 $MJkg^{-1}$of dry CR, respectively. Therefore, the hydrothermal process with maximum composition of biomass can use minimum hydrothermal process running required energy. When hydrothermal products are under water cooling system, then the product cooling process water can recover some heat and it can be used as the input water of the HT process. If this system is applied in a HT process then the HT process required energy will reduce. For a simple estimate of 80 °C of cooling process water can save hydrothermal input energy calculated from (4.51 × wt% of water × 55)/(wt% of dry biomass) in per kg dry biomass basis. Therefore, the energy requirement for a hydrothermal process of 240 °C for 30 min can use less energy of 4.71 $MJkg^{-1}$, 3.06 $MJkg^{-1}$, 2.23 $MJkg^{-1}$, 1.74 $MJkg^{-1}$ and 1.41 $MJkg^{-1}$ of dry CR, respectively for 5%, 7.5%, 10%, 12.5% and 15% CR (dry) composition in water. In this case the required net input energy can be calculated for these five compositions of CR to 13.79 $MJkg^{-1}$, 8.98 $MJkg^{-1}$, 6.57 $MJkg^{-1}$, 5.15 $MJkg^{-1}$, and 4.16 $MJkg^{-1}$ of dry CR, respectively.

5.2. Co-digestion of lignocellulosic biomass with other substrates as an opportunity

Two or more substrates mixing to enhance biogas production is a technique known as co-digestion. There is a potentiality to increase biogas production from high C/N ratio lignocellulosic biomass if it is co-digested with low C/N ratio substrates. Co-digestion of lignocellulosic biomass with animal waste can balance carbon and nitrogen ratio to optimize biogas production at a commercial level because mono-digestion produces low biogas for digester instability (Abouelenien et al., 2014). Cellulose content, hemicellulose content and C/N ratio of rice straw, wheat straw, corn stover and switch grass are 32%, 24% and 47; 38%, 21% and 60; 37%, 22% and 63; and 38%, 26% and 93, respectively (Karthikeyan and Visvanathan, 2012), which have high potential for biogas production with co-digestion of other suitable substrates. Biogas production in co-digestion of two biomass is shown in Table 8.

Lignocellulosic biomass is rich in cellulose and hemicellulose, which serves as a great potential for anaerobic digestion but their high value of C/N ratio and complexity of biomass structure (contains 10–25% lignin) inhibits anaerobic digestion process when it is used for mono-digestion (Sawatdeenarunat et al., 2015). Typical lignocellulosic biomass such as corn stover, wheat straw, switch grass and bagasse contain C/N ratio of 63, 60, 90 and 118, respectively (Kartikeyan and Visvanathan, 2012; Brown et al., 2012; Li et al., 2014). Co-digestion of hay with soybean processing waste at 25:75 ratio was investigated in a solid-state AD process for biogas production, which produced methane yield of 258 Lkg^{-1} VS. This co-digestion obtained 50% and 148% more biogas production compared to 100% hay and 100% soybean processing waste, respectively (Zhu et al., 2014). Co-digestion of barley straw with pig manure can produce 233.4 Lkg^{-1} VS methane but it can produce only192.0 Lkg^{-1} VS methane when it is co-digested with cow manure (Wei et al., 2014). Corn stover and dog food (expired) at equal ratio (1:1) can produce methane yield of 304.4 Lkg^{-1} VS, which led to an increase of 129% compared to corn stover alone and 9% compared to dog food digestion alone (Xu and Li, 2012). In the case of various crop residues anaerobic co-digestion with manure, MSW and slaughter house waste at equal ratio (25% each w/w) of individual substrate can produce 655 Lkg^{-1} VS methane (the highest) in thermophilic batch assays (Pagés-Díaz et al., 2014). Rice straw with swine manure, wheat straw with chicken manure, corn stover with chicken manure and crop silage with cow manure can produce 350, 235, 223–298 and 249 Lkg^{-1} VS methane, respectively in AD co-digestion process with optimum C/N ratio. In the case of mono-digestion, corn stover alone can produce 132 Lkg^{-1} VS methane (Brown et al., 2012), yard waste alone can

produce 41 Lkg^{-1} VS methane (Liew et al., 2012), grass silage alone can produce 60 Lkg^{-1} VS methane (Lehtomaki et al., 2008a, 2008b), switch grass alone can produce 117 Lkg^{-1} VS methane, wheat straw alone can produce 124 Lkg^{-1} VS methane (Brown et al., 2012) and leaves alone can produce 55Lkg^{-1} VS methane (Liew et al., 2012). However, several energy crops such as maize (corn), wheat, sorghum, sunflower and grass have the potential methane content of 291–338 Lkg^{-1} VS, 351–378 Lkg^{-1} VS, 286–319 Lkg^{-1} VS, 231–297 Lkg^{-1} VS and 286–324 Lkg^{-1} VS, respectively (Weiland, 2010). Lignocellulosic biomass, especially energy crops are mostly rich in carbohydrate, which means more carbon content (Ye et al., 2013; Giuliano et al., 2013) and animal waste such as chicken manure contains high organic nitrogen (Abouelenien et al., 2014; Li et al., 2014). Therefore, both lignocellulosic biomass and animal wastes contain inappropriate C/N ratio, which is responsible for low methane production in their mono-digestion. Co-digestion of lignocellulosic biomass with appropriate animal waste for optimum C/N ratio can maximize methane production (Ye et al., 2013). The yield of biogas from swine manure obtained the highest value when it was co-digested with three lignocellulosic biomasses such as corn stalk, wheat straw and oat straw by maintaining C/N ratio at 20 (Wu et al., 2010). One of the main reasons for higher methane production from co-digestion of manure with lignocellulosic biomass compared to manure alone is the increase in the degradable part of VS in substrate. The easily degradable portion of VS of animal eaten food is digested in the stomach of animals and the tough degradable portion of VS (lignin) stays in their manure. Therefore, when lignocellulosic biomass is mixed with manure, the easily degradable portion of VS of the mixture is increased (Lehtomaki et al., 2007). Food waste co-digestion with sewage sludge can produce a high yield of biogas of 708 Lkg^{-1} VS (Liu et al., 2012).

5.3. Conclusions and recommendations

Lignocellulosic biomass is a high potential feedstock of anaerobic digestion to produce methane but its high value of C/N ratio and complexity of biomass structure (contains 10–25% lignin) inhibit anaerobic digestion process when it is used for mono-digestion. Combined acid and hydrothermal pretreatment at a high temperature produces phenolic compounds, furfural and HMF, which are inhibitors to anaerobic digestion. But combined alkali and hydrothermal pretreatment at a suitable temperature can reduce this risk. Suitable combined pretreatment (two or more pretreatment methods) produces higher methane, reduces pretreatment severity and higher digestion of biomass compared to the use of a single pretreatment method. Anaerobic co-digestion of hydrothermally pretreated lignocellulosic biomass with another suitable nitrogen rich biomass has high potentiality to enhance biogas production for maintaining optimum C/N ratio. Intensive study about this type of co-digestion is needed.

The hydrothermal process of maximum composition of biomass can use minimum hydrothermal process input energy. The hydrothermal products' cooling water can recover some heat which can be used in the hydrothermal process to reduce input energy. Biochar produced in hydrothermal pretreatment process is a coal like product, which can be used as a potential substitute of coal. After separation of biochar, hydrothermal process water can be used for biomethane production to recover maximum bioenergy from a biomass where optimum hydrothermal process condition is important. A pretreatment process increases cost of anaerobic digestion plant and this cost is further increased when combined pretreatment is introduced. Additional equipment, materials, technology and resource persons are required. A techno-economical study is needed for single pretreatment, combined pretreatment and co-digestion of lignocellulosic biomass with various other nitrogen rich substrates.

Greenhouse biomass of low C/N ratio is favourable for AD but its complex structure with lignin needs proper pretreatment. However, pretreatment of greenhouse biomass in an optimum hydrothermal process for maximum biochar and biogas production, use of biogas in CHP system, and capturing of the exhaust CO_2 gas to use for greenhouse plants can reduce the green house operating cost. On the other hand, AD digestate is a liquid bio-fertilizer, which can be applied to greenhouse plants. Finally greenhouse can run with zero waste management strategy with minimum running cost, and reduce GHG gas emissions and climate change.

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